Ultrafast Photophysics of Matrix-isolated PAH Cations: ***Per aspera ad astra***

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Our studies of internal energy conversion in molecular systems of polycyclic aromatic hydrocarbons (PAHs) have unexpectedly led to new insights into astrochemistry. Molecules of PAHs missing a valence electron (radical cations) are thought to be responsible for diffuse interstellar bands (DIBs) commonly observed in star-forming clouds in our Galaxy. The identity of the DIB species is a century-old puzzle that is central to astrochemistry. The only information available to astronomers is IR emission and UV-vis absorption spectra that contain dozens of narrow, well-resolved lines. These lines are due to electronic transitions between the ground and excited states of PAH cations. To prove that these narrow lines are indeed from the PAH cations, better understanding of their relaxation dynamics is needed since the lifetime of a photoexcited state is uniquely related to the width of a spectral line associated with this state. These linewidths are being surveyed by astrophysicists, and they need information from experimenters to draw conclusions from their observations. To aid them in this important task, we have studied relaxation dynamics for photoexcited PAH cations using subpicosecond ($< 10^{-12}$ s) transient grating spectroscopy. The recovery kinetics for the ground states of PAH cations contain a fast (0.1-0.2 ps) and a slow (3-20 ps) components. We have shown that the fast component is due to electronic relaxation from a photoexcited state to a “hot” ground state and the slow component is due to vibrational energy transfer from this "hot" ground state to the solid matrix used to isolate and stabilize the PAH cations. Rapid deactivation accounts for remarkable photostability of PAH cations which explains their longevity and abundance in the interstellar environment and would account for 40-60% of the organic matter in the Universe. The observed lifetimes of the excited states compare favorably with the linewidth data for the 428 nm feature obtained by scientists at the University of Colorado – Boulder’s Center for Astrophysics and Space Astronomy (T. Snow et al.) and therefore give additional confirmation that PAHs are responsible for DIBs observed in star-forming clouds in our Galaxy.